Excimer Formation in Solutions of Vinylaromatic Polymers

AUTHOR(S):

Odani, Hisashi

CITATION:

Odani, Hisashi. Excimer Formation in Solutions of Vinylaromatic Polymers. Bulletin of the Institute for Chemical Research, Kyoto University 1974, 51(6): 351-372

ISSUE DATE:

1974-03-30

URL:

http://hdl.handle.net/2433/76511

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 51, No. 6, 1973

Review

Excimer Formation in Solutions of Vinylaromatic Polymers

Hisashi ODANI*

Received December 5, 1973

Excimer formation and fluorescence in solutions of vinylaromatic polymers have been reviewed. In fluorescence spectra of a number of polymer solutions lower energy band is assigned to fluorescence from an excimer state formed by the interaction of nearby chromophores on the same polymer chain. Mechanism of intramolecular excimer formation in polymer systems have been discussed in relation to local conformation and local motion of the polymer chain. Temperature dependence of fluorescence from fluid solutions of vinylaromatic polymers have also been discussed through kinetic considerations.

I INTRODUCTION

In concentrated or aggregated systems many planar aromatic hydrocarbon molecules in their first excited singlet state interact with unexcited molecules of the same species and produce excited dimers, which are stable in the electronically excited state only and dissociate in the ground state:

$$^1M^* + {}^1M \longrightarrow {}^1D^* .$$

These excited dimeric complexes are known as excimers. The term *excimer* was introduced by Stevens and Hutton[1] to distinguish the dimeric complex from the normal excited dimer of certain dyes which is produced by absorption of light from a stable dimeric ground state. The excimer behaves like a distinct molecular species, and it exhibits its own characteristic fluorescence and photophysical properties.

The excimer fluorescence was first reported by Förster and Kasper for concentrated solutions of pyrene.[2] They have found that, whereas the absorption spectrum remains unchanged, the violet, structured fluorescence of dilute solutions of pyrene is replaced by a broad, blue, structureless band as the concentration of pyrene is increased. At higher concentrations the excimer responsible for the blue fluorescence is formed collisionally from excited and unexcited pyrene molecules. According to cryoscopic data, the association of unexcited pyrene molecules does not occur even in the most concentrated solutions.

Since the discovery of excimer formation and fluorescence in pyrene solutions by Förster and Kasper, fluorescence from the excimer has been observed for a number of aromatic hydrocarbon molecules. Many studies, particularly by Birks and his school, have shown that the phenomenon of excimer formation and fluorescence is common to most aromatic hydrocarbons and their derivatives in fluid solutions, pure liquids and crystalline

* 小谷 壽: Laboratory of Polymer Solutions, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

states. These studies have been recently reviewed by Parker,[3] Förster[4] and Birks.[5,6] The reaction kinetics of excimer formation and dissociation, theoretical interpretations of excimer interaction in aromatic molecules, and photophysical processes involved excimers are discussed in detail in the reviews.

Apart from excimer formation in fluid solutions of low-molecular-weight aromatic hydrocarbon, excimer fluorescence has also been observed in aromatic polymer solutions. Systematic studies of excimer formation in macromolecular systems have been pioneered by Hirayama for styrene polymers.[7] He has identified the fluorescence at longer wavelength of atactic polystyrene in dilute solutions at room temperature as due to excimers, formed mainly by *intramolecular* interaction between adjacent phenyl groups in the same polymer chain. Excimers can also be produced in solids, or in highly concentrated solutions, of vinylaromatic polymers. In these cases, neighboring aromatic groups in adjacent polymer chains interact with each other and form excimers.

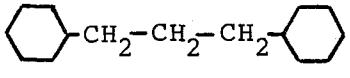
In this paper an attempt has been made to compile relevant papers on the excimer formation and fluorescence in fluid solutions of vinylaromatic polymers and to point out some of the important aspects of the phenomenon. Discussions concerning photophysical processes observed with solids and glassy solutions of vinylaromatic polymers will be excluded. In these cases the interested reader is referred to the recent publication[8] of the topic.

II INTRAMOLECULAR EXCIMER FORMATION

II. 1 Model Compounds for Polymers

Before discussing excimer formation and fluorescence of vinylaromatic polymers in fluid solution, we shall first describe excimer formation in dilute solution of related model compounds.

In dilute solution of monomeric aromatic compounds the average separation distance of solute molecules is great and excimer formation will be occurred only to a very slight extent compared with that at higher concentrations. This is because in order to form the excimer an excited molecule should encounter a second solute molecule within a distance of 3–4 Å during the lifetime of the excited state. If however, two, or more, aromatic residues are flexibly liked to each other by a chain of saturated carbon atoms, the probability of encounter between the aromatic residues is greatly increased and an appreciable proportion of excited aromatic residues is expected to be capable of forming excimers intramolecularly even at higher dilutions. Hirayama[7,9] has found that this is indeed the case in dilute solutions of diphenyl alkanes, triphenyl alkanes, and ditolyl alkanes in which the phenyl groups along the main alkane chain are separated by *three* carbon atoms. Figure 1 shows the fluorescence spectrum of nitrogenated solutions of 1,3-dipheynlpropane



in cyclohexane and *p*-dioxane at room temperature. The spectrum consists of two emission bands appearing in the regions of 280 and 330 nm. The structured band at higher energy is the mirror image of the molecular absorption spectrum, and it

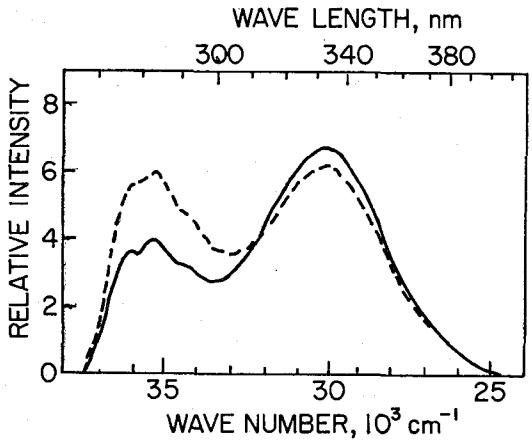


Fig. 1. Fluorescence spectra of 10^{-2} M nitrogenated solutions of 1,3-diphenylpropane in cyclohexane (solid line) and *p*-dioxane (broken line) at room temperature (after Hirayama[7,9]). Concentration in units of benzene rings.

corresponds to the fluorescence of "*monomer*" phenyl group. The lower energy structureless band has no counterpart in the absorption spectrum, and it is attributed to the fluorescence from *intramolecular excimer*.

Hirayama has measured fluorescence spectra of sixteen diphenyl and triphenyl alkanes and indicated that the intramolecular excimer fluorescence is observed with, and only with, compounds in which n, the number of carbon atoms separating the phenyl groups, is equal to *three*.[9] He has suggested two alternative explanations of this "$n=3$" rule based on considerations of molecular configuration.

In the first explanation the excimer configuration is assumed to be a parallel sandwich type with a certain degree of overlapping of the two π orbitals. Without the deformation of tetrahedral bond angles of alkane chains, the parallel face-to-face arrangement is impossible for $n=1$ or 2. For $n=3$, the parallel configuration can be obtained with a *trans* form of the propane chain, if two phenyl groups can approach a mutual distance $R_m=2.54$ Å. For $n=4$, 5, and 6 the parallel arrangement is possible only for $n=5$, if alkane chains are assumed to take an extended *trans* form, a configuration of minimum energy for normal alkanes. In this case, however, R_m is 5.08 Å for $n=5$, which may be considered to be too great separation for two phenyl groups to exhibit excimer behavior. Therefore, it may be concluded that formation of this type of excimer is possible only when $n=3$.

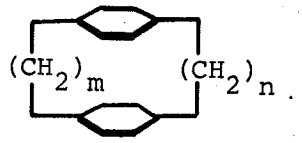
The strict requirement for the excimer configuration assumed in the first explanation is made less severe in the second explanation. It is assumed that the excimer may be formed with greater separation of two phenyl groups than 3.2 Å but sufficiently small, or with partial overlap of electron clouds without necessitating an exact face-to-face parallel arrangement. Except $n=3$, however, two phenyl groups cannot approach each other close enough to form an excimer, because of the limitation of bond angles (for $n=1$ and 2), or to configurational instability (for $n=4$, 5, and 6) of the main alkane chains.

It is also indicated from measurements of fluorescence spectra of diphenyl and triphenyl alkanes that in the $n=3$ compound the fluorescence quantum yield of the monomer phenyl group is considerably reduced relative to the $n\neq3$ compounds.[9] This is due to the

intramolecular excimer formation, in a manner analogous to concentration quenching observed in pyrene solutions. Information about the reaction kinetics of the process has been obtained from studies of quenching of the fluorescence emissions by dissolved oxygen,[9] and it is concluded that the excimer formation process can be described in a similar manner to normal intermolecular excimer formation in solutions of monomeric aromatic compounds such as pyrene. The kinetics for excimer formation will be discussed in detail later.

Formation of the intramolecular excimer with 1,3-diphenylpropane in solution has been confirmed by Vala and others.[10] Again the $n=3$ rule is exhibited in their study by the absence of excimer emission band in observed fluorescence spectra with 1,2-diphenylethane and 1,4-diphenylbutane solutions.

Intramolecular dimer fluorescence is also observed in some of the paracyclophane series:[10]

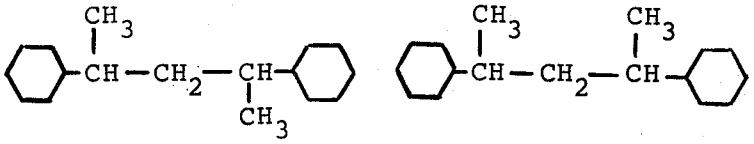


Vala and others have measured absorption and emission spectra of four compounds of the paracyclophane series. In 2,2′-paracyclophane ($m=n=2$) and 4,4′-paracyclophane ($m=n=4$), the two aromatic groups are in a sandwich type arrangement, and only a structureless emission band is observed. In the former compound, however, the observed absorption spectrum is distorted significantly from that characteristic of monomer phenyl group, and it is considered that the fluorescence is that of an excited dimer, rather than excimer, though the peak of the broad band shifts even farther to the red than the monomer fluorescence band observed for the related compounds. On the other hand, the absorption spectrum of 4,4′-paracyclophane is similar to that of ethylbenzene, and the broad emission band is attributable to excimer fluorescence of this compound. On the basis of normal bond angles and lengths, Cram and others[11] have calculated the separation of two phenylene groups to be 3.73 Å. Vala and others have understood the observed excimer fluorescence in this compound to be a consequence of the vibrationally induced decrease in the separation of two chromophore groups.

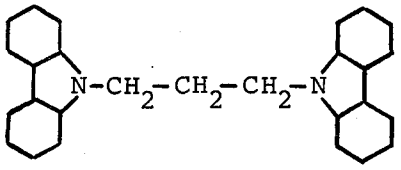
The fluorescence spectra of 4,5′-paracyclophane ($m=4$ and $n=5$) and 6,6′-paracyclophane ($m=n=6$) display only the monomer fluorescence band. In these compounds the extra methylene groups in the bridges of the paracyclophane separate two phenylene groups to such a distance that excimer formation is impossible by the vibrational motion of the aromatic groups. Thus, it has been deduced from fluorescence measurements with the paracyclophanes that intramolecular excimer formation is possible for phenylene groups in a parallel face-to-face arrangement with separation of two chromophores equal to, or less than, 3.73 Å.[10] This value of the separation, and also those discussed by Hirayama[9] for excimer formation in alkanes containing phenyl groups, are well compared with that of the equilibrium intermolecular separation, 3.34 Å, which is determined from the excimer fluorescence spectra of pure, single pyrene crystals.[5,6]

Excimer fluorescence has also been observed in dilute solutions of *dl*-2,4-diphenylpentane (A) and *meso*-2,4-diphenylpentane (B),[12] and those of 1,3-bis(N-carbazolyl) propane (C)[13] at room temperature. The former compounds are model compounds of

styrene polymers and the latter is that of poly(N-vinylcarbazole). Again approximately parallel-stacked, face-to-face arrangement with separation of 2–3 Å between two chromophore groups has been suggested in the reports.



(A) (B)



(C)

II. 2 Polymers

Excimer fluorescence from fluid solution has been observed for a number of vinylaromatic polymer systems: polystyrene[7,14~19] (PS), poly(1-vinylnaphthalene)[10,19~24] (P1VN), poly(2-vinylnaphthalene)[19,22,25] (P2VN), poly(acenaphthylene)[19,22~24,26,27] (PACN), poly(N-vinylcarbazole)[28~30] (PVCA), poly(vinyltoluene)[7] (PVT), poly(arylnaphthalene)[22] (PARN), and poly(1-vinylpyrene)[31] (P1VP). In many vinylaromatic polymers, such as PS, P1VN, and P2VN, excimer formation in dilute solution at room temperature is interpreted as the result of *intramolecular* excited-state interaction between adjacent chromophores in the same chain.

In below, fluorescence from solutions of vinylaromatic polymers will be discussed in two subsections which are arbitrarily divided for convenience' sake. First we will present experimental results of fluorescence spectra of solutions of PS, which is taken as one of the typical example of flexible polymers, and discuss the experimental support of the assignment for excimer fluorescence in the spectra. Also will be described excimer fluorescence from solutions of poly(vinylnaphthalene) (P1VN and P2VN), poly(α–methylstyrene) (PMS), and styrene copolymers. Fluorescence behavior of other class of vinylaromatic polymers will be shown in the subsequent subsection, and experimental investigations with PACN and PVCA will be described mostly therein.

(*A*) *Polystyrene, Poly(α-methylstyrene), and Poly(vinylnaphthalene)*

Figure 2 shows fluorescence spectra of atactic polystyrene in *p*-dioxane at room temperature, measured under aerated condition.[32] Several important features of the spectra should be noted. First, all the fluorescence spectra given in the figure contain two bands: a smaller band in the region about 285 nm, and a larger broad band in the longer wavelength region with a maximum at 333 nm. The overall shape of each fluorescence spectrum is quite similar to that of the model compound, 1,3-diphenylpropane, shown in Fig. 1. As mentioned previously, the higher energy band of low-molecular-weight compound is the mirror image of the molecular absorption spectrum, and is attributed to molecular fluorescence originating from nonassociated excited chromophores. The shape of the smaller band of atactic PS is also that would be expected from the mirror-image

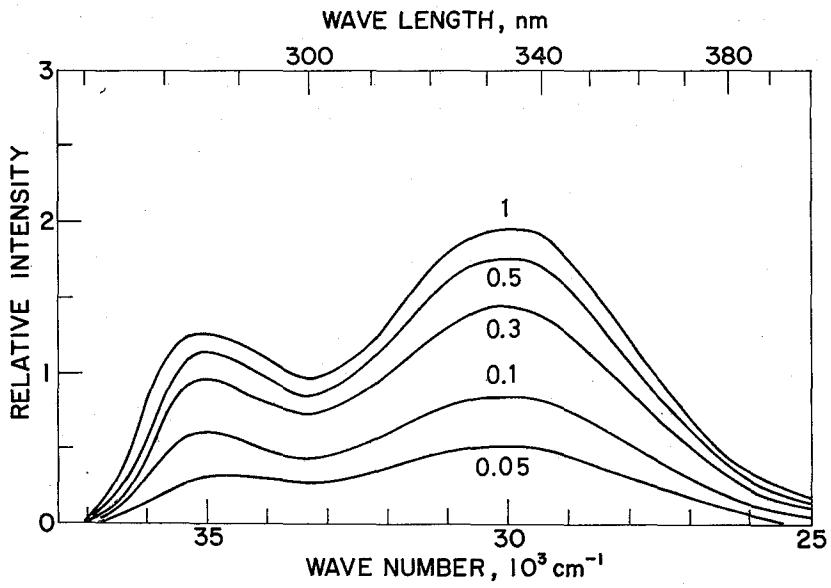


Fig. 2. Fluorescence spectra of aerated solutions of atactic polystyrene (narrow molecular weight distribution) in 1,2-dichloroethane at 25°C (after Odani and Pardhan[31]). Concentrations in g/dl.

correspondence to the absorption spectrum, though the fine structure in the absorption spectrum has been lost in the shorter wavelength band. The absorption spectrum of PS is almost identical to that of ethylbenzene, as found initially by Smakula.[33]

The remarkable similarity is also exhibited between the shapes of the longer wavelength band of PS and that of the model compound. Furthermore, the peak of the band of each fluorescence spectrum appears at almost the same wavelength as that observed in solutions of the model compound. For diphenyl and triphenyl alkanes the structureless, broad band of lower energy is assigned to intrachain excimer fluorescence arrising from an excited phenyl group in the singlet state interacting with another phenyl group in the ground state.

Next, it can be seen from the figure that the spectral distribution of the fluorescence spectra does not vary with concentration of PS. The independent nature on concentration over the wide region of polymer concentration has been established not only for PS,[7,10]* but also for P1VN,[10,23] P2VN,[19] and PMS,[34] except for region of very high concentration. In fluid solutions of PS the wavelength regions of the two bands are also independent of the molecular weight of the polymer and the type of solvent.[7,32]

Finally, the maximum of the longer wavelength band appears about 5000 cm^{-1} to the red of the higher energy band. The magnitude of the shift is well compared with that for model compounds of the vinylaromatic polymer,[5,9] and also that for low-molecular-weight aromatic hydrocarbons.[5,6]

* For PS, the independence on concentration of the positions of the two emission maxima on wavelength axis has been established in all the experimental results referred to above except for those given in one report.[18] The latter observations which exhibited concentration dependent behavior of the peak of lower energy band, however, are now considered to be fallacious and would be resulted from some ill condition in measurements.

From the concentration behavior of the fluorescence spectra of PS and also from comparison of the spectra of PS with those of one- and two-chromophore model compounds, Hirayama[7,9] and Vala and others[10] have concluded that in dilute solutions the short wavelength band and the broad, longer wavelength band are assigned respectively to *molecular fluorescence* from the individual phenyl group and to *intrachain excimer fluorescene* between neighboring phenyl groups in the same chain. These authors have considered that excimers are formed in solution between nearest, or next-nearest, neighboring groups, and not between far-distant neighbors whose proximity and interaction are dependent on the chain folding back on itself. The fluorescence studies of solutions styrene copolymers, such as copolymers of styrene and methyl methacrylate, have demonstrated that excimer fluorescence is related to the number of styrene pairs and not to the number of styrene units in the copolymer.[7,19,21,35~37] Experimental results with styrene copolymers appears to give evidence in favor of the interpretation of excimer formation mechanism mentioned above.

In this connection, it would be of interest to compare fluorescence behavior of solutions of atactic PS with that of isotactic PS. If excimer is formed in solution between nearest, or next-nearest, neighbors in the same chain as proposed by Hirayama[7,9] and Vala *et al.*,[10] then, one may expect that variety of the stereochemical structures of the polymer chain might be reflected on observed fluorecence behavior. Hirayama has found for very dilute solutions in 1,2-dichloroethane that the spectral distribution of the fluorescence of atactic PS does not differ from that of isotactic PS.[7] Similar results have been reported by Vala and others.[10] The latter authors have noted, however, that the ratio of excimer to monomer fluorescence intensity, I_D/I_M, for atactic PS is slightly greater than that for isotactic PS. In contrast to the findings, Longworth observed that the value of I_D/I_M in dilute solution of isotactic PS in cyclohexane is greater than that of atactic PS by a factor of about four at room temperature (*ca.* 25°C). In the report an idea that light absorption would produce a transient local melting of the helix of an isotactic PS chain has been suggested to explain the observed facts.

With regard to the influence of variation of the stereo-regularity of polymer chain on the efficiency of excimer formation, interesting results have been obtained recently in solutions of PMS.[34] The stereo-regularity of PMS is controlled by the polymerization procedure, such as choice of catalyst and solvent, and temperature. Furthermore the microstructure of prepared samples can easily be determined by high resolution nmr analysis. The cationically polymerized PMS samples give fairly low values of isotactic–dyad content, whereas samples of relatively higher isotactic-dyad content are yielded by the anionic polymerization technique. Figure 3 exhibits fluorescence spectra of 0.1 g/dl solutions of four different samples of PMS in *p*-dioxane under aerated condition.

In PMS solutions higher energy band at about 290 nm and lower energy band at about 335 nm, both are in essentially identical wavelength regions with PS, are assigned to monomer and excimer fluorescence, respectively. Anionically polymerized samples, BB 8 and BB 13*, exhibit relatively high efficiency of excimer formation. On the other hand, the intensity of higher energy band is greater than that of lower energy band in solutions

* These samples were polymerized in tetrahydrofuran at −78°C using n-BuLi as catalyst. Values of M_v of BB 8 and BB 13 are 2.71×10^6 and 4.75×10^4, respectively. Isotactic-dyad content of the former is 20% and that of the latter is 31%.

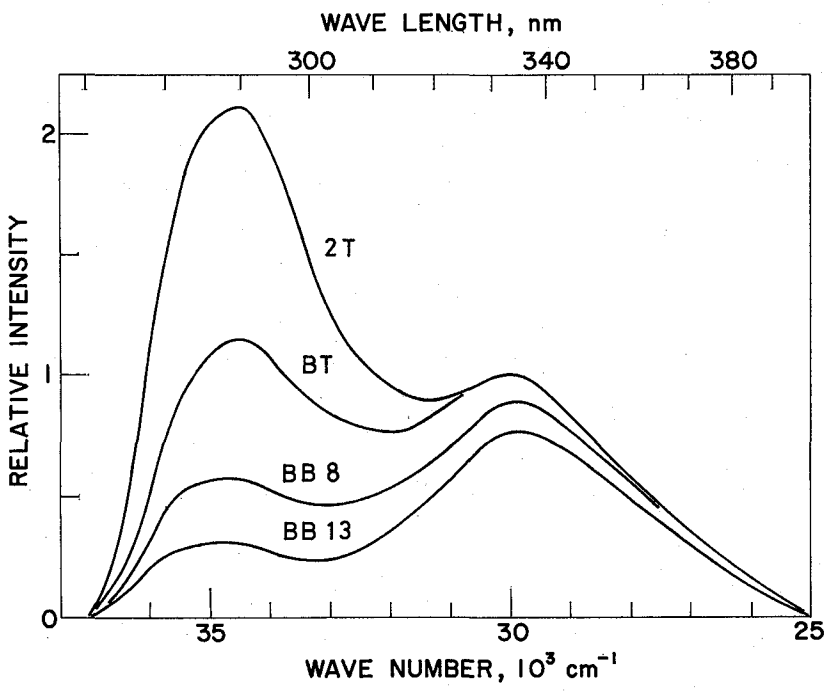


Fig. 3. Fluorescence spectra of 0.1 g/dl aerated solutions of poly(α-methylstyrene) in *p*-dioxane at 25°C (after Odani *et al.*[34]). BB 8 and 13 are anionically polymerized, and BT and 2T are cationically polymerized asmples.

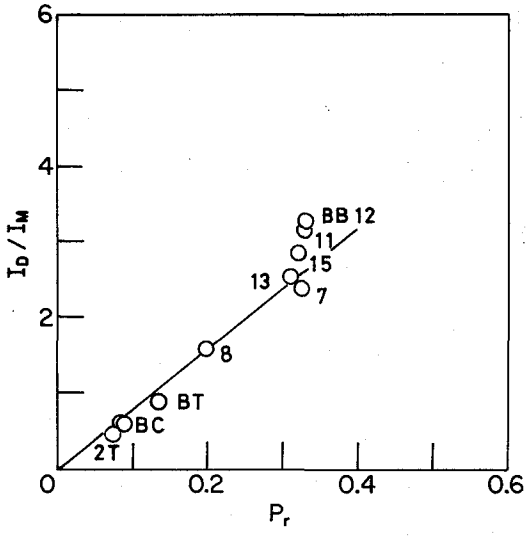


Fig. 4. Dependence of the ratio I_D/I_M on isotactic-dyad content P_r for 0.1 g/dl solutions of poly(α-methylstyrene) in *p*-dioxane (after Odani *et al.*[34]). Anionically polymerized samples: BB 7, 8, 11, 12, and 13. Cationically polymerized samples: BC, BT, and 2T.

of PMS samples prepared by cationic polymerization, 2T and BT,* especially in the former sample. The dependence of the ratio, I_D/I_M, on the probability of finding isotactic-dyad along the polymer chain, P_r, is given in Fig. 4. It is seen that the dependence can be represented by a straight line which passes the origin of the plot. The difference in the effect of steric regularity of the polymer chain on fluorescence behavior between the systems of PS and PMS is rather surprising, and needs some explanation. In later, will be described interpretation based upon considerations of molecular motions of polymer chain in solution and also of reaction kinetics for the excimer formation processes. It has been reported for solutions of P1VN that variation in the local stereochemical structures has little influence on the efficiency of excimer formation.[21]

Apart from the discussion of the effect of microstructures on fluorescence from solutions of PS and PMS, much the same independence of the spectral distribution of fluorescence on concentration as PS solutions has been found also for other class of vinylaromatic polymers; PACN,[23,24] PVT,[7] and P1VN.[30] Again, the conclusion that the lower energy band in the fluorescence spectrum most likely originates from intrachain effect may follow from the observed independence of the ratio, I_D/I_M, on concentration in a variety of solutions of vinylaromatic polymers.

As described in the foregoing lines, the comparison of fluorescence spectra of solutions of vinylaromatic polymers with those of the model compounds provides profound support for the basis of the assignment and the interpretation of the double fluorescence from polymer solutions, especially those of the excimer band at longer wavelength. This means that the basis of steric considerations of the excimer configuration in the vinylaromatic polymer may be assumed to be not very different from that in low-molecular-weight model compounds. In vinylaromatic polymers, such as PS, PMS, P1VN, and P2VN, which bear not so bulky chromophore unit in side-groups, the assumption could be justified. However, in solutions of other class of vinylaromatic polymers which have bulky substituent groups, such as PVCA, it is questioned whether the favorable arrangement of aromatic rings for excimer formation can be met by adjacent chromophore groups on the same chain. The similar doubt may also be thrown upon excimer formation in solutions of PACN. This polymer consists of monomeric units in which two adjacent carbon atoms in the backbone chain join to a naphthalene ring at its 1 and 8 positions. Therefore, the face-to-face interaction between nearest, or next-nearest, neighbors in the same chain may be expected to be most unlikely. The fluorescence behavior of these polymers will be discussed in the next subsection.

(*B*) *Poly(N-vinylcarbazole) and Poly(acenaphthylene)*

As described in Section II.1, intramolecular excimer formation in model compounds of poly(N-vinylcarbazole) has been demonstrated for solutions of 1,3-bis(N-carbazolyl) propane.[13,30] On the other hand, no excimer band has been observed in fluorescence spectra of solutions of N-ethylcarbazole and 1,4-bis(N-carbazolyl) butane.[30] The results

** Sample 2T was polymerized by using $TiCl_4$ as catalyst and water as cocatalyst. Polymerization was performed in toluene at −78°C. Sample BT was prepared in 5 : 3 (by volume) mixture of toluene and *n*-hexane at −78°C using $BF_3O(C_2H_5)_2$ as catalyst. Values of M_v are 1.05×10^5 and 1.10×10^6, and those of isotactic-dyad content are 7.5 and 13.5%, for 2T and BT, respectively. The author wishes to express his gratitude to Dr. Hans von Euler for the gift of the sample BT.

clearly indicate that in the series of carbazole-group containing compounds excimers can be formed only the interacting chromophores are separated by three carbon atoms (the "$n=3$" rule).

Klöpffer studied the fluorescence from benzene solutions of PVCA at various concentrations and found that excimer fluorescence is independent of concentration.[28] The results have been interpreted by him as that the face-to-face arrangement between two neighboring side groups in the same chain, which is favorable to excimer formation, is encountered by a suitable change in conformation of the polymer chain in solution. In a recent report, Nishijima and his co-workers have shown that the quantum yield of the excimer emission of PVCA is higher than that of 1,3-bis(N-carbazolyl) propane.[30] They have noticed in the report that, though the "$n=3$" rule is obeyed in the series of compounds bearing carbazole groups, a possibility of excimer formation between carbazole groups separated more than three carbon atoms can not be excluded completely in solution.

Temperature effect on fluorescence from 2-methyltetrahydrofuran solutions of PVCA were studied by David and others in the region from the liquid nitrogen temperature to 425°K.[29] The experimental results have been analyzed in terms of a kinetic scheme for excimer formation, which will be presented in Chapter IV, and has been suggested the existence of two different types of excimer, in lower and higher temperature regions, respectively. These two succesive excimers have been considered by them as to be resulted from a conformational change of the rigid and bulky chain. They have deduced from the observation that the conformational change would occur between 143° and 295°K. Above 295°K, the binding energy of the second type excimer, which is considered to correspond to the conformation of PVCA chain at the higher temperatures, has been evaluated as 2.8 kcal mole^{-1}. As will be described in detail later, the value is well compared with those reported for solutions of other vinylaromatic polymers, such as polystyrene and poly(vinylnaphthalene).

All the interpretations of excimer formation in fluid solutions of PVCA referred to above, thus, may allow for us to draw the same conclusion that, irrespective of the stiffness of the chain, intrachain interaction between excited and unexcited carbazole groups in the same chain is the origin of the observed excimer fluorescence from PVCA solutions. As noted by David and others,[29] the rigidity of the PVCA chain is clearly demonstrated by higher values of the steric factor σ, 2.85 or 2.8, for PVCA;[38] σ is defined by

$$\sigma^2 = \langle L^2 \rangle_0 / \langle L^2 \rangle_{0f}$$

where $\langle L^2 \rangle_0$ is the mean-square displacement length of the chain in the unperturbed state and $\langle L^2 \rangle_{0f}$, that corresponding to completely free internal rotations but to fixed valence angles. Values of σ were found to be 2.2 and 1.6 for polystyrene and polyethylene, respectively.[39]

However, for PVCA solutions, whether the interaction between nearest, or next-nearest, neighbors on the same chain will be dominant in the excimer formation seems to be still open for future studies. As described above, in solutions of flexible vinylaromatic polymers, such as PS, it has been concluded that the excited aromatic group forms an excimer predominantly with its first-neighbor unexcited group. In this connection, a very recent study by Yokoyama and others of fluorescence from solutions of carbazole containing copolymers should be noted.[40] Excimer formation between nearest neighboring groups has been inferred in their results.

The nature of excimer interaction in solutions of poly(acenaphthylene) is not clear at all at the present time. This is because characteristics of fluorescence behavior have not yet been well established for PACN solutions. As an instance the observed dependence of excimer emission on concentration may be quoted. Marked discrepancy in the concentration dependence can be seen among experimental results obtained by various research groups, and quite different interpretations of mechanism of excimer formation have been derived therefrom. The observations of excimer fluorescence in PACN solutions may be introduced conveniently by dividing into two groups. This will be done below according to the observed dependence of spectral distribution of fluorescence on concentration of PACN.

David and his co-workers have revealed that the ratio of excimer to monomer fluorescence intensity, I_D/I_M, is independent of concentration for 2-methyltetrahydrofuran solutions of PACN at room temperature.[23] This behavior is quite the same as observed for PS and other flexible vinylaromatic polymers. They have deduced from the observations that excimer in the PACN solutions is attributable to intramolecular interaction between two naphthalene rings in the same chain.

The view that excimer formation in PACN solutions can be interpreted as the intramolecular process has again emphasized in their subsequent paper.[24] In the report excimer formation between an excited chromophore and its next-nearest neighbor in the same chain has been conceived for PACN solutions at higher temperatures. While, for P1VN solutions at room temperature excimer formation has been interpreted as due to intramolecular interaction between the nearest neighboring naphthalene rings. They have explained the observed large difference in the ratio I_D/I_M between PACN and P1VN systems in terms of the above-mentioned difference in type of chromophore pairs of excimers; that is, chromophore pairs formed between next-nearest neighbors in the former and between nearest neighbors in the latter. The observed values of I_D/I_M are 1.3 and 12.6 for PACN and P1VN, respectively at room temperature.[23]

The independence of excimer fluorescence on concentration has also been indicated by Samedova and others for benzene solutions of PACN.[27] They have concluded from the result that the interaction may take place between chromophores on the same chain.

The observations by Samedova and others, which show an effect of molecular weight on excimer emission from PACN solutions, may be noted. They observed that the intensity of excimer fluorescence increased by almost a factor of ten with increasing molecular weight of the polymer from 60,000 to 550,000. The similar dependence of spectral distribution on molecular weight has also been observed by Nishijima and others for fluorescence from dichloromethane solutions of P1VN.[20,21] However, the latter observations are limited to only the region of molecular weight lower than 62,000, corresponding to the region of the average degree of polymerization lower than forty. For PS solutions, as mentioned previously, the spectral distribution and the intensity of excimer fluorescence have found to be independent of molecular weight in the region of higher molecular weight.[7,32] The increase in excimer fluorescence from PACN solutions with increasing molecular weight has been interpreted by Samedova and others as to indicate that probability of contact between naphthalene rings is enhanced with increasing molecular weight. Though the concentration independent behavior of the ratio I_D/I_M[23] and that of excimer fluorescence[27] have been demonstrated for PACN solutions, the

effect of molecular weight on excimer formation seems to suggest that one should interpret very carefully the process of excimer formation in the system.

Contrary to the observations by European research groups,[23,27] which are in favor of the interpretation that excimers in PACN solutions are formed mostly by intramolecular interaction between chromophores, Nishijima and his co-workers have shown that the ratio I_D/I_M depends strongly on concentration even in dilute solutions.[22] They have studied the fluorescence from benzene solutions of PACN in concentration region up to 50 wt.% and found that the ratio $I_D/(I_D+I_M)$ increases steadily with increasing concentration. The rate of the increase in the ratio is higher at lower concentrations than in the region of medium concentration. The results have been interpreted as to show a prevailing role of intermolecular interaction between chromophores in the process of excimer formation, though the intramolecular formation of excimers has not been excluded in very dilute solutions.[22] A reason for the sharp contrast between experimental findings of the two research groups, David *et al.* and Nishijima *et al.*, is not known to us at the present time. Nishijima and others suggested that the intermolecular excimer formation in PACN solutions would be resulted from enhanced overlapping of the polymer coils with increasing concentration. Also has been noticed by them much less value of I_D/I_M for PACN than that for P1VN. They have found that the ratio for PACN is only about 1/40 of that for P1VN in solutions of the same solvent, dichloromethane. The result may be compared with that obtained by David and others described above. Nishijima and others have considered that this low value of the ratio may be ascribed to less freedom of rotation of the naphthalene rings in polymer chain of PACN than those in P1VN.

As mentioned before, judging from the molecular structure of PACN the face-to-face interaction between nearest neighboring chromophores in the same chain is considered to be most unlikely. Nevertheless, all the experimental results cited above have indicated that excimer fluorescence is emitted from dilute solutions of the polymer. Also all explanations given by different research groups seem to agree with one another in respect to recognizing dominant role of intramolecular interaction between naphthalene rings for the process of excimer formation in PACN solutions, at least in dilute solutions. Besides the interpretation by David and others of intramolecular interaction between next-nearest neighbors mentioned above, Schneider and Springer have considered that intramolecular interaction may occur between chromophores on adjacent turns of the polymer coil in dilute solutions.[26] Quite the same view has been presented by Fox and his colleagues together with an alternative explanation for excimer formation in PACN solutions, in which occurrence of some type of agglomeration in the polymer chain is suggested.[19]

III EXCIMER FORMATION AND MOLECULAR MOTION

We have purposely delayed until this point the discussion of local segmental motion of the polymer chain. Though it has been emphasized in the preceding sections that *equilibrium* local conformation of the polymer chain plays the very important role in the excimer interaction, many experimental results suggest that local motions of the polymer chain contribute much to the process of intramolecular excimer formation. For

instance, as noted by Nishijima,[35] relatively high efficiency of excimer fluorescence from vinylaromatic polymers in solution compared with that from low-molecular-weight compounds may be understood by taking account of micro-Brownian motion of polymer chains.

Intramolecular excimer is expected to be formed if an excited chromophore can find out its partner in face-to-face arrangement at a distance of the order of 3–4 Å during its lifetime. In other words, if the excited lifetime is longer than rotational, or other internal, relaxation time, then excimer fluorescence due to intramolecular interaction will be observed in solutions of the vinylaromatic polymer. For the low-molecular-weight model compound, the prerequisite is fulfilled by very fast transition from one configuration into the other isomers. That is, the radiative lifetime of aromatic compounds of low molecular weight is in the order of magnitude of 10^{-9}–10^{-8} sec,[5,6] while values of the order of 10^{-10} sec are estimated for the lifetime of rotational isomer.[41] However, the lifetime conditions are considered to be not always met by the polymer system. Therefore, close inspection of the lifetime conditions is needed in interpreting mechanism of excimer formation in the polymer system. The lifetime conditions will be examined below for fluid solutions of PS.

Hirayama[7] and other researchers[10,17] have reported that the fluorescence decay time for PS in solution at room temperature is about 2×10^{-8} sec. Though the decay time is not a direct measure of the lifetime of chromophore in the excited state, the lifetime of chromophore in the excimer state would be longer than the measured decay time.

Information about the local motions of a polymer chain in solution can be obtained from acoustic, esr, fluorescence depolarization, and nmr measurements. However, until the present time we have been able to find out from literature a few data of the relaxation time for local motions of PS molecule in solution. Values of the order of magnitude of 5×10^{-9}–5×10^{-7} sec have been given in a paper of Hässler and Bauer for the relaxation time of rotational-isomeric transition in the polymer chain of PS.[42] A three-state model for the transition has been presented by them based upon acoustic studies of PS solutions.[42,43] Also, they have suggested that simultaneous rotation of two backbone single bonds and the penyl group is involved in the transition between two different conformations. In some instances the spatial arrangement of adjacent phenyl groups in the same chain, which is favorable to excimer interaction, may be attained by the reorientation of each phenyl group. If the polymer chain of PS in solution is in the random coil state, the time required for the reorientation is reported to be in the order of magnitude of 10^{-9}–10^{-8} sec.[42,44~47]

The examinations of the lifetime conditions mentioned above lead us to the conclusion that the requirement may be fulfilled by the fluid solutions of PS at room temperature. Thus, even when the predominant population of lower energy conformer(s), in which the phenyl groups are in spatial arrangement not favorable for excimer formation, is expected in the polymer chain from steric considerations, the appropriate local conformation for excimer formation can be attained by local segmental motion within the radiative lifetime of the excited phenyl group, if the potential barrier between conformers is not fairly high. In fact, Longworth and Bovey have shown that for 2,4-diphenylpentanes, model compounds of PS (*cf.* Section II.1), isomers favorable for excimer formation are higher energy conformers, two *meso* isomers and *dl* isomer.[12] Nevertheless, predominance of excimer fluorescence in PS solutions at room temperature can be resulted from the

lifetime conditions together with not so high value of the potential barrier between rotational isomers. For *meso*-2,4-diphenylpentane Gorin and Monnerie have evaluated the potential barrier between two stereoisomers (g^-t and tg^+) as to be about 3 kcal mole.$^{-1}$ [48] From ultrasonic relaxation studies of PS solutions Bauer and others have found the total potential difference of 7.5 kcal mole^{-1} between the two-fold upper level and the lower level of their model.[42,43] The activation energy of the order of 4–5 kcal mole^{-1} has been found for local segmental motion in polymers of styrene derivatives in solution by dielectric[45,46,50] and esr[51] measurements.

The effect of temperature on the lifetime conditions will be discussed here briefly. The temperature dependence of the process of excimer formation will be described in detail later. The radiative lifetime of the excited state has generally been found to be independent of temperature.[37] The relaxation times for local motions of the polymer molecule, on the other hand, are wellknown to be dependent of temperature as well as those for motions of whole molecule. At very low temperatures the relaxation time becomes much longer than that at room temperature, probably by several orders of magnitude, and the lifetime conditions will be not satisfied by the polymer system concerned. Hence, it is anticipated that emission from the polymer consists almost entirely from monomer fluorescence. In fact, this is the case for fluid solutions of PS, but as will be mentioned later somewhat different behavior is observed for other class of vinylaromatic polymers.

In Section II.2 (A), the difference in the effect of stereoregularity on fluorescence behavior has been noticed between solutions of PS and PMS. A suggestion how to answer the question why the linear relationship between the ratio of excimer to monomer fluorescence and isotactic-dyad content is exhibited by PMS solutions in contrast to PS solutions could be given by considering large difference in the potential barrier between conformers. For 2,4-dimethyl-2,4-diphenylpentane, which is a model compound for PMS, Gorin has estimated the potential barrier between conformers to be higher than 15 kcal mole.$^{-1}$ [52] From this quite high value of the potential barrier one may imagine that short scale backbone rotational motion would be much more hindered in a chain of PMS than that of PS. In this connection, it would be of interest to note nmr studies of PMS by Oudin and others.[53] They have deduced from the temperature dependence of nmr signal that in PMS molecule enhancement of the amplitude of motion of phenyl groups occurs independently of conformational change in main chain. On the other hand, a transition in motion of phenyl groups of PS has been found to be dependent of transition in local rotational motion of backbone.[54]

The decay time of fluorescence from P1VN in solution has been reported to be about 3×10^{-8} sec.[10] Though data of the rotational relaxation time have not yet been reported for P1VN solutions, the lifetime conditions would probably be met in solutions of P1VN at room temperature. For other class of vinylaromatic polymers, such as PVCA and PACN, still reliable data of the excited lifetime, as well as those of the relaxation time for local segmental motion, are not available at present. However, it appears that the observed excimer fluorescence from PVCA solutions, which is probably attributable to interaction between nearest neighbors in the same chain, might suggest fulfilment of the lifetime conditions by the polymer molecule in some environment.

IV KINETIC CONSIDERATION OF INTRAMOLECULAR EXCIMER FORMATION

The general kinetic scheme for excimer processes in polymer solutions are:

$^1M + h\nu \longrightarrow {}^1M^*$	excitation	I_0	(1)
$^1M^* \longrightarrow {}^1M + h\nu_M$	monomer fluorescence	k_{FM}	(2)
$^1M^* \longrightarrow {}^1M$	internal conversion	k_{GM}	(3)
$^1M^* + {}^1M \longrightarrow {}^1M + {}^1M^*$	singlet migration	k_{MM}	(4)
$^1M^* + {}^1M \longrightarrow {}^1D^*$	excimer formation	k_{DM}	(5)
$^1D^* \longrightarrow {}^1M + {}^1M + h\nu_D$	excimer fluorescence	k_{FD}	(6)
$^1D^* \longrightarrow {}^1M^* + {}^1M$	excimer dissociation	k_{MD}	(7)
$^1D^* \longrightarrow {}^1M + {}^1M$	dissociative internal conversion	k_{GD}	(8).

The schematic energy level diagram is shown in Fig. 5. The symbols and nomenclature are essentially those used by Birks.[5,6] More generally, photophysical processes in which the triplet excited chromophore ($^3M^*$) and excimer ($^3D^*$) are involved, are taken into consideration. Particularly, for emission from solids, or glassy solutions, of vinylaromatic polymers these processes should be taken into account for interpretation of experimental results. However, usually neither phosphorescence nor delayed fluorescence is detectable in solutions of vinylaromatic polymers at room temperature. Therefore these processes are excluded from the discussion given below.

A few comments will be made here for the process of singlet migration. In solids, or in glassy solutions, the important contribution of the process to the efficiency of excimer emission has been suggested by many researchers. In fluid solutions, however, there exists considerable divergence of view as to the contribution of intramolecular energy migration. For PS solutions, for instance, Hirayama has considered that the excitation energy migration from segment to segment does not occur in a chain molecule.[7] Contrary to this view it has been argued that even in fluid solutions the energy migrates through the phenyl groups of a chain of PS until a site favorable to excimer formation is encountered.[17] From the discussion given in the preceding chapter, for PS system molecular motion ensures that many such sites are attainable in fluid solutions at room temperature. Hence, it may be considered that in fluid solutions of PS the energy migration along the polymer chain is a minor process and negligible in interpreting mechanism of excimer formation, except for at fairly low temperatures. However, singlet energy transfer in a chain has been inferred in aerated solutions of P1VN at room temperature.[19]

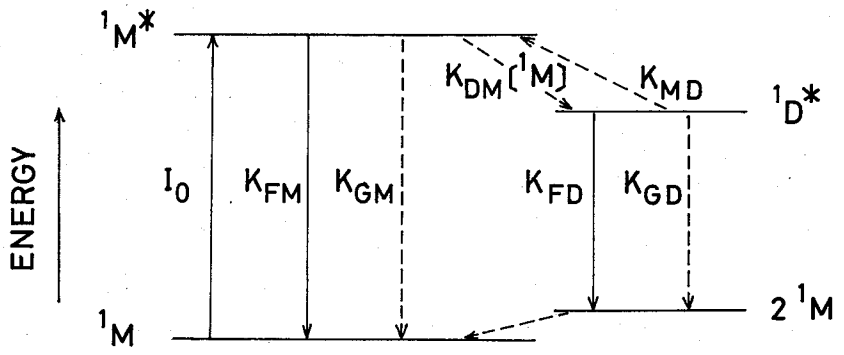


Fig. 5. Schematic energy level diagram for excimer formation.

For the model compounds for polymers values of rate parameters appeared in the general kinetic treatment have been evaluated by Hirayama.[9] Discussions with respect to this subject, however, will be omitted in this review.

Now we will discuss the mechanism of excimer formation and fluorescence in terms of general scheme of reaction kinetics given above. In order to interpret fluorescence behavior of PS solutions, a reaction mechanism has been proposed by Hirayama[7,9] based upon considerations of local conformation and lifetime conditions mentioned before. Vala and others suggested quite the similar mechanism to that of Hirayama.[10]

The first step in the excimer processes is the excitation of independent individual chromophores (process (1)). If intramolecular excimer formation process (5) occurs with an efficiency very close to 100%, then, the monomer fluorescence occurs exclusively via a path in which the monomer fluorescence process (2) follows the excimer dissociation process (7). That is, in this case the immediate return of $^1M^*$ to ^1M is entirely prohibited, and monomer fluorescence is dependent on excimer formation. This mechanism is called here Mechanism I according to Vala and others.[10]

However, it is possible that the monomer fluorescence process (2) may occur immediately after excitation and before the excimer formation. In this instance, the observed monomer fluorescence may be assumed to be the sum of the fluorescence from originally excited $^1M^*$ which is not taken part in the excimer formation process (5) and from $^1M^*$ regenerated by the excimer dissociation process (7). Monomer fluorescence from the former path is independent on process (5). This mechanism is designated Mechanism II. In this mechanism the excimer formation occurs competitively with the direct radiative return of excited chromophore to the ground state.

Here it is worthwhile to notice that the reverse of the process (6) is not included in either mechanism. This is because, as mentioned previously, no evidence for excimerlike formation in the ground state has been observed in the absorption spectra of the polymer solutions concerned.

For the interpretation of observed fluorescence behavior, a way of choice among the two mechanisms will be provided by the following investigations, *i.e.* quenching of fluorescence by dissolved oxygen and temperature dependence of fluorescence behavior. In Mechnism I, if we compare fluorescence spectra of oxygenated, or aerated, solutions with those of nitrogenated solutions the effect of oxygen quenching on the monomer and excimer fluorescence be approximately the same, since the monomer fluorescence in this mechanism is completely due to radiative transition of $^1M^*$, which has been formed by the excimer dissociation process (7), to ^1M.

On the other hand, according to Mechanism II the excimer band intensity is expected to be quenched by dissolved oxygen to a much larger extent than that of the monomer band. The lifetime of an excited chromophore may be considered to be substantially short owing to the efficient competition of the excimer formation process. Since the fluorescence quenching by oxygen is the collisional process between an excited fluorescent molecule and oxygen molecule, the more effective in quenching the longer the lifetime of the excited chromophore group is.

The effect of oxygen quenching on the fluorescence spectra of solutions of PS and PMS in *p*-dioxane is exhibited in Table I.[34] In the third and fourth columns, are given values of the ratio, I_D/I_M, observed respectively in argonated, or nitrogenated, solutions

Table I. The Effect of Oxygen Quenching on the Fluorescence Spectra of Solutions of PS and PMS in p-dioxane (after Odani *et al.*[34]).

Sample	Temp. °C	I_D/I_M		Ratio
		Ar, N_2	O_2	
atactic PS	45	3.18	1.64	1.9
isotactic PS	45	8.25	5.72	1.4
anionic PMS				
BB 13	25	2.50	2.72	0.92
BB 8	25	1.64	1.28	1.3
cationic PMS				
BT	25	0.96_1	0.72_4	1.3
BC	25	0.61_6	0.46_8	1.3
2T	25	0.53_7	0.38_0	1.4

Concentration; 0.1 g/dl

and oxygenated solutions. "Ratio", which is given in the fifth column, is the ratio of I_D/I_M in argonated solution to that in oxygenated solution. The greater value of "Ratio" than unity, therefore, corresponds to an observation that the quenching of excimer band is larger than that of monomer band. It is noted in the table that the value of "Ratio" in solutions of atactic PS is the largest and is decreasing in the order isotactic PS, cationic PMS, and anionic PMS. For PS, values of I_D/I_M under nitrogenated and oxygenated conditions, and also those of "Ratio" calculated from these values, are well compared with those of Vala and others,[10] obtained in 1,2-dichloroethane at room temperature.

Hirayama[7] and Vala *et al.*[10] have concluded that the results of oxygen quenching of fluorescence from solutions of PS and P1VN give evidence to support the Mechanism II. But, values of "Ratio" close to unity for PMS solution might indicate that Mechanism I would be favorable to interpret the process of excimer formation in this system. It has been found that essentially the same value of "Ratio" is obtained with PMS solutions in various solvents.[34]

Another information that will help in answering which mechanism should be employed in the explanation of observed fluorescence behavior of vinylaromatic polymer solutions may be provided observations of fluorescence at very low temperatures. If we recall the discussion of the important role of molecular motions in the excimer formation process, according to Mechanism II one will be able to expect disappearance of the excimer band at very low temperatures. Since, according to Mechanism II, the competition between monomer fluorescence and excimer formation processes should result lowering, very much lowering, of efficiency of excimer formation at very low temperatures by suppressing local segmental motions. On the other hand, Mechanism I predicts that no marked decrease in the relation between intensities of excimer and monomer fluorescence will be observed by lowering temperature of the system concerned.

Observations of fluorescence from PS and P1VN in glassy medium by Hirayama[7] and Vala *et al.*[10] have revealed that fluorescence spectra at liquid nitrogen temperature contain only the monomer fluorescence band and the excimer band disappears almost completely. The results, together with those of the effect of oxygen guenching upon

fluorescence spectra mentioned above, lead us to the conclusion that Mechanism II is preferred, at least in the system of PS and P1VN. For PMS, however, it was noted that oxygen quenching on fluorescence behavior is different from that in solutions of PS and P1VN. Furthermore, fluorescence spectra of PMS solutions the excimer band is still observed at very low temperatures, though the relative intensity of the excimer fluorescence to the monomer fluorescence is reduced to a certain extent.[34] The similar behavior has been observed by David and others with solutions of P1VN, PACN, and PVCA.[24,29] Figure 6 illustrates the temperature dependence of the fluorescence spectra of dilute solutions of P1VN in 2-methyltetrahydrofuran.[24] It is seen that even at 120°K the excimer band still exists as a shoulder in the tail of fluorescence spectra in the region of longer wavelength. The features of fluorescence from PMS solutions described above might suggest that Mechanism I would be satisfactory in explaining simultaneously the observed oxygen quenching and the dependence on temperature, on concentration also, together with the observed influence of the stereo-regularity upon fluorescence behavior (*cf.* Section II.2 (A)).

As has been suggested by Hirayama,[9] a more direct way of choosing between Mechanism I and II would be to measure the decay time of the monomer fluorescence. For example in PS solutions, by Mechanism I the decay time is expected to be about 2×10^{-8} sec, while by Mechanism II the decay contour should contain two components decaying with the above-mentioned two different decay times. Unfortunately reliable data which allow us to use in analysis along this line has not yet been available at present.

The general kinetic scheme for excimer processes given in the foregoing lines provides

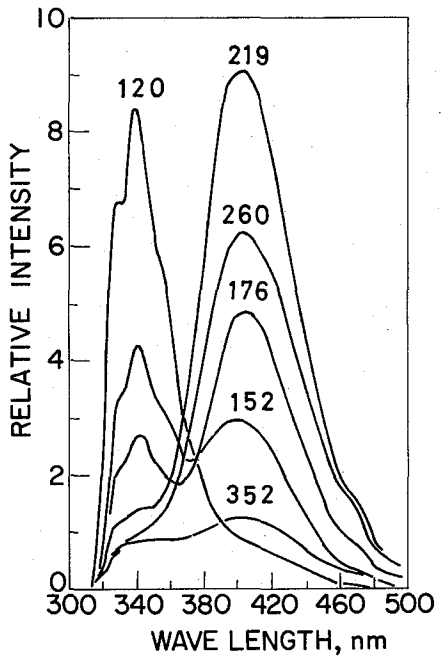


Fig. 6. Temperature dependence of fluorescence spectra of 10^{-3} M solutions of poly(1-vinylnaphthalene) in 2-methyltetrahydrofuran (after David *et al.*[24]). Concentration in units of naphthalene rings.

us a method to analyze the observed temperature dependence of fluorescence from polymer solutions. In what follows the analysis according to the general kinetic treatment, which has been done mostly by the research group of David and his co-workers, will be described, and apparent activation energy estimated by the kinetic treatment will be shown for various vinylaromatic polymer systems. David and others have investigated extensively the temperature dependence of fluorescence spectra of solutions of vinylaromatic polymers.[24,29] Many studies have also been undertaken to elucidate the effect of temperature on fluorescence behavior of solutions of PS, P1VN and P2VN.[19,25] In the studies of temperature dependence of excimer formation in P2VN solutions, Harrah has developed similar treatment as David and others.[25]

If a photostationary state is verified for the excited monomer $^1M^*$ and excimer $^1D^*$, the ratio of monomer to excimer fluorescence intensity is given by the relation

$$\frac{I_M}{I_D} = \frac{k_{FM}(k_D+k_{MD})}{k_{FD}k_{DM}} \qquad (9),$$

where, k_D is the sum of k_{FD} and k_{GD}. It has generally found that k_{FM} and k_{FD} is independent of temperature.[37] Thus if the following two assumptions,

(1) $k_{MD} \ll k_D$

(2) k_D is independent of temperature,

are valid, the activation energy for excimer formation, E_{DM}, can be evaluated from a slope of the linear potion at low temperatures in plots of log (I_M/I_D) against the reciprocal of temperature. As an example, the plots for solutions of P1VN in 2-methyltetrahydrofuran and in ρ-dioxane are shown in Fig. 7. The validity of the above assumptions was discussed by David and others.[24] As a consequence of the discussion, these assumptions have been verified for P1VN and PACN solutions at low temperatures. Also it has been demonstrated that k_D is independent of temperature for the systems concerned. Accordingly, under the conditions concerned one can evaluate the value of E_{DM} from the slope of the linear portion of the plots at lower temperatures.

The two assumptions mentioned above are shown to be verified also for other systems, and we can evaluate values of E_{DM} of these systems by the method suggested by David

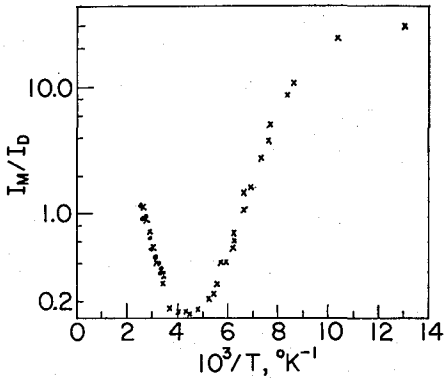


Fig. 7. Temperature dependence of the ratio I_M/I_D for 10^{-3} M solutions of poly(1-vinylnaphthalene) in 2-methyltetrahydrofuran (●) and in p-dioxane (×) (after David *et al.*[24]). Concentration in units of naphthalene rings.

Table II. Activation Energies for Excimer Formation, E_{DM}, in Dilute Solutions.

Polymer	Solvent	E_{DM} (kcal mole^{-1})	Ref.
PS			
atactic PS	1 : 1 DE/THF	1.5	19
	1 : 2 DE/THF	2.1	34
isotactic PS	THF	1.7	34
P1 VN	1 : 1 DE/THF	2.3	19
	MTHF	2.7	24
P2 VN	MTHF	3.5	55
	n-propyl benzene	3.6	25
	3 : 2 DE/THF	4.5	22
PMS			
BB 13	1 : 2 DE/THF	1.1	34
BB 8	1 : 2 DE/THF	1.4	34
BT	1 : 2 DE/THF	1.2	34
2T	1 : 2 DE/THF	1.4	34
PACN	MTHF	0.8	24

DE/THF: mixture of diethylether and tetrahydrofuran
MTHF: 2-methyltetrahydrofuran THF: tetrahydrofuran

and others. Table II summarizes all available data of E_{DM} up to present. Method of evaluating the value of E_{DM} adopted by Fox and others,[19] however, is somewhat different from that described above. It is noted that lower values are obtained for PMS than those for PS, P1VN, and P2VN. Quite low value for PACN is rather surprising. Vinylaromatic polymers which exhibit lower values of E_{DM} are those displaying fluorescence characteristics for which Mechanism I was preferred.

In the temperature range where the minimum value of I_M/I_D is obtained in the plots shown in Fig. 7, it has been observed a slowing down of the rate of decrease of the monomer fluorescence.[24] David and his co-workers has explained this behavior in terms of excimer dissociation. The binding energy of the excimer is obtained from the negative slope of the plots at higher temperatures, and values of 3.6 and 2.1 kcal mole^{-1} are estimated by them for P1VN and PACN, respectively. As mentioned previously, the behavior of PVCA solutions is quite different from that of P1VN and PACN. Two minima corresponding to two different types of excimer have been displayed in plots of log (I_M/I_D) versus 1/T.[29] The binding energy for the high temperature excimer in solution has been determined above 295°K as 2.8 kcal mole^{-1}.

Concluding Remarks

The mechanism of intramolecular excimer formation, proposed by Hirayama and Vala and others, has undoubtedly provided a way of understanding of observed fluorescence behavior in a number of vinylaromatic polymer solutions, at least in a qualitative manner. Many experimental results cited in this review also suggest that valuable information about the local conformation and molecular motion of aromatic polymers and copolymers may be obtained from fluorescence studies. However, in order to gain insight

into the nature of electronic phenomena occurring in solutions of aromatic polymers, future studies are needed. Though information about local conformation and segmental motion, upon which the present interpretation of the excimer processes is based, is still limited at the moment, further investigations, such as precise decay time measurements and studies of the fluorescence behavior in solutions of related copolymers having different types of sequence distribution in the chain, will help us very much in interpreting the observed behavior on the molecular level. Furthermore, accelerated increase in quantitative knowledge of local conformation and molecular motion of the polymer chain is expected to improve much our understanding of this subject within next few years.

ACKNOWLEDGMENTS

The author wishes to thank to Professor Michio Kurata for his helpful discussions. Invaluable suggestions given by Professor Stig Claesson, University of Uppsala, during his stay at our Institute in 1972 are also gratefully acknowledged.

REFERENCES

(1) B. Stevens and E. Hutton, *Nature*, **186**, 1045 (1960).
(2) Th. Förster and K. Kasper, *Z. Electrochem., Ber. Bunsenges. Phys. Chem.*, **59**, 976 (1955); *Z. Phys. Chem. (Frankfurt)*, **1**, 275 (1954).
(3) C. A. Parker, "Photoluminescence of Solutions," Chap. 4, Elsevier, Amsterdam, 1968.
(4) Th. Förster, *Angew. Chem. Internat. Ed.*, **8**, 333 (1969).
(5) J. B. Birks, *Progress in Reaction Kinetics*, **5**, 181 (1970).
(6) J. B. Birks, "Photophysics of Aromatic Molecules," Chap. 7, Wiley-Interscience, London, 1970.
(7) F. Hirayama, "Energy Transfer and Quenching in Plastic Scintillators," thesis, University of Michigan, 1963.
(8) R. B. Fox, *Pure Appl. Chem.*, **30**, 87 (1972).
(9) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
(10) M. T. Vala, Jr., J. Haebig, and S. A. Rice, *ibid.*, **43**, 886 (1965).
(11) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954).
(12) J. W. Longworth and F. A. Bovey, *Biopolym.*, **4**, 1115 (1966).
(13) W. Klöpffer, *Chem. Phys. Lett.*, **4**, 193 (1969); *Ber. Bunsenges. Phys. Chem.*, **74**, 693 (1970).
(14) S. S. Yanari, F. A. Bovey, and R. Lumry, *Nature*, **200**, 242 (1963).
(15) J. W. Longworth, *Biopolym.*, **4**, 1131 (1966).
(16) F. Hirayama, L. J. Basile, and C. Kikuchi, *Mol. Cryst.*, **4**, 83 (1968).
(17) F. Heisel and G. Laustriat, *J. Chim. Phys. Physicochim. Biol.*, **66**, 1881 (1969).
(18) T. Nishihara and M. Kaneko, *Makromol. Chem.*, **124**, 84 (1969).
(19) R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, **57**, 534 (1972).
(20) Y. Nishijima, K. Mitani, S. Katayama, and M. Yamamoto, *Repts. Progr. Polym. Phys. Japan*, **13**, 421 (1970).
(21) Y. Nishijima, *Nippon Kagakusen-i Kenkyusho Koen Shu (Ann. Rep. Res. Inst. Chem. Fibers, Japan)*, **27**, 1 (1970).
(22) Y. Nishijima, *ibid.*, **28**, 13 (1971); Y. Nishijima, M. Yamamoto, S. Katayama, K. Hirota, Y. Sasaki, and M. Tsujisaki, *Repts. Progr. Polym. Phys. Japan*, **15**, 445 (1972).
(23) C. David, M. Lempereur, and G. Geuskens, *Eur. Polym. J.*, **8**, 417 (1972).
(24) C. David, M. Piens, and G. Geuskens, *ibid.*, **8**, 1019 (1972).
(25) L. A. Harrah, *J. Chem. Phys.*, **56**, 385 (1972).
(26) F. Schneider and J. Springer, *Makromol. Chem.*, **146**, 181 (1971).
(27) T. G. Samedova, G. P. Karpacheva, and B. E. Davydov, *Eur. Polym. J.*, **8**, 559 (1972).
(28) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).

(29) C. David, M. Piens, and G. Geuskens, *Eur. Poly. J.*, **8**, 1291 (1972).
(30) Y. Nishijima, Y. Sasaki, K. Hirota, and M. Yamamoto, *Repts. Progr. Polym. Phys. Japan*, **15**, 449 (1972).
(31) J. R. McDonald, W. E. Echols, T. R. Price, and R. B. Fox, *J. Chem. Phys.*, **57**, 1746 (1972).
(32) H. Odani and S. Pardhan, to be published.
(33) A. Smakula, *Angew. Chem.*, **47**, 777 (1934).
(34) H. Odani, M. Uno, N. Nemoto, and M. Kurata, in preparation.
(35) Y. Nishijima, *J. Polym. Sci., C***31**, 353 (1970).
(36) H. Odani and N. Nemoto, to be published.
(37) C. David, M. Lempereur, and G. Geuskens, a reference cited in Ref. 24 as "to be published."
(38) N. Kuwahara, S. Higashida, M. Nakata, and M. Kaneko, *J. Polym. Sci., A2*, **7**, 285 (1969); G. Sitaramajah and D. Jacobs, *Polymer*, **11**, 165 (1970).
(39) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).
(40) M. Yokoyama, Y. Tanamura, R. Ogawa, Y. Yano, and R. Mikawa, presented at the 22nd Polym. Symp., Soc. Polym. Chem. Japan, Nov., 1973.
(41) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," Chap. 3, Interscience Pub., New York, 1963.
(42) H. Hässler and H.-J. Bauer, *Kolloid Z., u. Z. Polym.*, **230**, 194 (1969).
(43) H.-J. Bauer and M. Immendörfer, *Disc. Faraday Soc.*, **49**, 238 (1970).
(44) F. A. Bovey, G. V. D. Tiers, and G. Filipovich, *J. Polym. Sci.*, **38**, 73 (1969).
(45) A. M. North and P. J. Phillips, *Trans. Faraday Soc.*, **64**, 3235 (1968).
(46) B. Baysal, B. A. Lowry, H. Yu, and W. H. Stockmayer, in "Dielectric Properties of Polymers," F. E. Karasz, Ed., Plenum Press, New York, N.Y., 1971, p. 329.
(47) W. H. Stockmayer and K. Matsuo, *Macromolecules*, **5**, 766 (1972).
(48) W. Ludlow, E. Wyn-Jones, and J. Rassing, *Chem. Phys. Lett.*, **13**, 477 (1972).
(49) S. Gorin and L. Monnerie, *J. Chim. Phys. Physicochim. Biol.*, **67**, 869 (1970).
(50) G. P. Mikhailov, A. M. Labanov, and M. P. Platanov, *Polym. Sci. U.S.S.R.*, **9**, 2565 (1967).
(51) A. T. Bullock, J. H. Butterworth, and G. G. Cameron, *Eur. Polym. J.*, **7**, 445 (1971).
(52) S. Gorin, *J. Chim. Phys. Physicochim. Biol.*, **67**, 878 (1970).
(53) J. C. Oudin, C. Nöel, and N. Platzer, *C. R. Acad. Sci. Paris, Ser. C*, **270**, 194 (1970).
(54) C. Nöel, N. Platzer, and A. Levy, *ibid.*, **269**, 1095 (1969).
(55) A. J. H. Al-Wattar and M. D. Lumb, *Chem. Phys. Lett.*, **8**, 331 (1971).